THE PAPER MAKING PROPERTIES OF STRAW HOLOCELLULOSE[1]

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Abstract

Fibrous holocellulose pulps were prepared in approximately quantitative yield from flax shives and wheat, oat, and fiber flax straw that had been macerated in a buhrstone mill and delignified by sodium chlorite. Paper hand sheets that were formed from pulps subjected to prolonged beating were glassinelike in character. Strength of all straw holocelluloses developed slowly on beating. All papers had relatively low densities compared with the usual values for papers from wood pulps. Tear resistance was initially low for all straw holocelluloses, especially flax shives, and decreased with beating. Color reversion, due almost entirely to light, was rapid in all test sheets. Possible uses for straw holocellulose papers are suggested, although, at present, the process is too expensive to be commercially feasible.

Introduction

Recent methods of preparing holocellulose in quantity have permitted investigation of the physical characteristics of papers containing the entire carbohydrate fraction of the cell wall (1, 8, 14, 16). Retention of the hemicellulose fraction of wood greatly increases the yield of pulp without impairing its paper making qualities. Jayme *et al.* (6) have made test sheets of good mechanical properties from aspen holocellulose. Studies on spruce holocellulose by Houtz and Kurth (5) showed that the presence of polyuronide hemicelluloses and cellulosans led to the development of a gelatinous hydrate on beating, and the glassine-type paper formed had remarkable strength characteristics. Investigation of white spruce holocellulose by Hajny and Ritter (3) showed that it had a high content of undegraded alpha-cellulose. They recommended removal of the hemicellulose fractions to give pulps with the desired characteristics for any particular purpose. Contrary to the statement of Holmberg and Jahn (4) that a true holocellulose cannot be prepared from softwoods, Lovell (8) has reported preparation of holocellulose from hemlock and slash pine with only slight loss. While holocelluloses from nonwoody plant materials have been prepared by methods involving acid chlorite (1, 2), chlorine–ethanolamine (11), and chlorine–pyridine (17), only Schenck and Kurth (11) have made a study of the paper making properties of holocellulose isolated from wheat straw. The straw holocellulose, unlike that of wood, developed strength very slowly on beating. No study has been found of the paper making properties of straw holocellulose prepared by the acid chlorite procedure.

The present paper deals with an investigation into the preparation of four straw holocelluloses by the acid chlorite method, their conversion to pulp stock and paper sheets, and an evaluation of the paper quality by physical tests. Wheat, oat, and flax straws were investigated because they are the commonest types and readily available; flax shives were studied because they are a by-product for which uses are being sought.

Experimental and Results

Raw Materials

Sound mature wheat and oat straws threshed from the 1946 crop were used. Owing to handling, most of the loose chaff and broken particles were absent from these straws. Occasional heads and kernels were removed by hand. Fiber flax was carefully freed of head and root structures. Flax shives were used directly as received from a flax processing plant. All materials were analyzed for moisture, lignin, ash, and Cross and Bevan cellulose by standard TAPPI methods (12). The results are given in Table I, *A*.

TABLE I

COMPOSITION OF STRAWS AND THEIR HOLOCELLULOSE FRACTIONS, % (ALL MATERIALS REPORTED ON AN OVEN-DRY BASIS)

	Wheat	Oats	Fiber flax	Flax shives
A. Straw				
Lignin (ash free)	21.21	19.21	22.54	30.11
Ash	6.89	8.95	3.52	1.46
Cellulose	54.9	49.6	52.4	48.2
*Hot water solubles	10.22	12.87	11.03	2.13
B. Holocellulose				
Yield	77.9	80.2	79.2	72.8
Lignin (ash free)	2.46	2.37	4.05	4.80
Ash	4.17	2.62	3.11	3.92
Cellulose	74.9	75.1	70.1	68.0

* *Extraction temperature, 75° C.*

Mechanical Pulping of Straw

Mechanical pulping of the straws was necessitated by the failure of acid chlorite delignification to effect any separation of cellulose fibers as occurs in most chemical pulping procedures. Acid chlorite holocellulose retains the physical characteristics of the original straw and cannot be satisfactorily pulped by the usual beater treatment. Preliminary mechanical pulping of the straws by maceration in ball mills, rod mills, and Waring blendors was not satisfactory owing to formation of a high proportion of fines and lack of breakdown of nodular structures. Test sheets of paper made from pulps prepared by these means contained an objectionable number of 'shives'. It was found that a buhrstone mill shredded the straw to a relatively fine fibrous pulp.

The pulping procedure finally evolved was as follows. About 1500 gm. of air-dry straw was chopped into pieces about ½ to 1 in. in length by means of a

commercial feed cutter.   The cut straw was then steeped for four to five hours in 30 liters of water at 75° C. to promote softening for the milling operation and to remove dirt particles and water soluble materials.   The steep water was removed by straining through cloth and the straw was thoroughly washed.   The wet material was then fed directly by hand into a 36 in. buhrstone mill.   Clearance of the moving stone during milling was adjusted arbitrarily to produce a uniform pulp.   Water at the rate of 4 to 5 liters per min. was fed in with the straw.   The pulp was recovered on a 48 mesh screen, and squeezed out, and recovered by hand.   Owing to lack of proper screening equipment, the loss of fiber in the milling operation was about 15 to 20% of the straw.   The wet pulp was not allowed to dry out before being delignified.

Preparation of Straw Holocellulose

The method used for preparation of holocellulose was an adaptation of Wise's analytical procedure using acid chlorite (16) and has been described previously by the authors (1).   The wet pulp was diluted to a consistency of 5% with water and subjected to delignification treatments for one hour at 75° C. using 30 gm. of sodium chlorite and 2.4 ml. of glacial acetic acid per 100 gm. of dry straw pulp.   Three successive treatments were used for wheat and oat straw; five were necessary for fiber flax and shives.   The pulps were then freed of their solutions by spinning in a perforated centrifuge bowl lined with fine filter cloth, and washed with distilled water until chloride-free. They were stored in the wet state until made into paper.   The yields of crude holocellulose and their lignin, ash, and cellulose contents are given in Table I, *B*.

Beater Tests

The holocellulose pulps were diluted to a 1.5% consistency and processed in a 1.5 lb. standard laboratory type Valley beater.   Preliminary tests showed that the usual side arm loading caused too drastic cutting action on the fibers so all experiments were done with 1 kgm. loadings.   Samples were withdrawn at 10 min. intervals for freeness tests according to TAPPI Standard T227 *m*-46.   Hand sheets were prepared for physical tests and optical tests by TAPPI standards T205 *m*-45 and T218 *m*-46 respectively.

Physical Tests on Paper

The hand sheets were conditioned for 24 hr. at 70° F. and 50% relative humidity according to TAPPI Standard T402 *m*-44.   The physical properties that were determined by TAPPI Standard T220 *m*-46 were as follows: basis weight, density, burst factor, tear factor, and breaking strength. The thickness of four sheets was measured with a Schopper automatic micrometer (accurate to 1/1000 in.) and the results divided by 4.   Printing opacity, which is the ratio of R_1, the reflectance of a single sheet backed with black, to R_z, the reflectance of a pile of sheets, was determined with a General Electric reflection meter.   The observed readings for the various sheets were calculated to a standard sheet weight of 1.2 gm.   Brightness was measured with a General Electric reflection meter according to T452 *m*-42.   The results of the physical tests are given in Tables II, III, IV, and V.

TABLE II

PHYSICAL PROPERTIES OF PULP MADE FROM WHEAT STRAW HOLOCELLULOSE

Beating time, min.	Freeness, (Canadian standard), ml.	Basis wt. gm./sq. m.	Density, gm./ml.	Burst factor, gm./sq. cm./ gm.	Tear factor, 100×gm./ gm.	Breaking length, m.	Printing opacity $\frac{R_1}{R_z}$	G.E. brightness at 458 $m\mu$, %
0	724	70.3	0.43	10.6	40.9	3909	0.750	66.1
10	677	67.0	0.45	12.3	38.1	4259	0.816	68.2
20	669	68.7	0.49	18.2	36.1	4573	0.765	68.4
30	560	71.3	0.53	20.8	33.4	5358	0.709	65.2
40	550	70.0	0.56	28.2	33.5	6631	0.820	62.2
50	520	68.2	0.58	31.3	33.4	7171	0.881	65.4
60	473	68.5	0.62	36.2	28.0	7293	0.800	63.1
70	448	68.5	0.64	41.3	28.0	7345	0.830	65.3
80	429	68.2	0.65	43.5	27.3	7852	0.852	61.3
90	344	69.3	0.69	44.5	26.7	8082	0.661	61.6

TABLE III

PHYSICAL PROPERTIES OF PULP MADE FROM OAT STRAW HOLOCELLULOSE

Beating time, min.	Freeness, (Canadian standard), ml.	Basis wt., gm./sq. m.	Density, gm./ml.	Burst factor, gm./sq. cm./ gm.	Tear factor, 100×gm./ gm.	Breaking length, m.	Printing opacity $\frac{R_1}{R_z}$	G.E. brightness at 458 $m\mu$, %
0	706	66.1	0.50	8.8	36.0	3463	0.736	61.6
10	677	67.0	0.45	12.8	39.7	4259	0.780	62.1
20	635	66.5	0.50	15.5	38.5	4558	0.820	62.4
30	607	65.4	0.46	15.8	37.4	4638	0.792	62.3
40	592	65.2	0.50	19.3	35.4	5579	0.740	62.2
50	565	64.9	0.50	21.3	34.3	6101	0.680	61.8
60	514	65.6	0.55	26.6	32.6	6204	0.724	60.5
70	485	65.2	0.56	30.8	30.5	6837	0.746	60.2
80	447	64.7	0.62	34.9	27.4	7715	0.680	56.9

TABLE IV

PHYSICAL PROPERTIES OF PULP MADE FROM FIBER FLAX HOLOCELLULOSE

Beating time, min.	Freeness, (Canadian standard), ml.	Basis wt., gm./sq. m.	Density, gm./ml.	Burst factor, gm./sq. cm./ gm.	Tear factor, 100×gm./ gm.	Breaking length, m.	Printing opacity $\frac{R_1}{R_z}$	G.E. brightness at 458 $m\mu$, %
0	466	68.0	0.26	4.5	47.0	1731	0.880	70.9
10	374	70.6	0.33	6.6	47.3	2528	0.795	67.2
20	289	69.6	0.35	8.3	40.3	3075	0.802	67.5
30	221	69.6	0.39	10.4	37.2	3331	0.810	69.0
40	176	71.3	0.38	11.0	37.8	3755	0.874	66.9
50	128	67.2	0.42	13.6	31.2	5045	0.887	67.0
60	98	72.4	0.45	15.6	27.5	5175	0.820	57.6
70	68	65.9	0.46	17.0	22.1	5415	0.848	62.4
80	53	64.6	0.51	20.8	24.8	5414	0.632	64.0

TABLE V

PHYSICAL PROPERTIES OF PULP MADE FROM FLAX SHIVES HOLOCELLULOSE

Beating time, min.	Freeness, (Canadian standard), ml.	Basis wt., gm./sq. m.	Density, gm./ml.	Burst factor, gm./sq. cm./ gm.	Tear factor, $100 \times$ gm./ gm.	Breaking length, m.	Printing opacity $\dfrac{R_1}{R_2}$	G.E. brightness at 458 $m\mu$, %
0	448	65.4	0.34	6.9	19.0	1746	0.848	70.8
10	368	67.5	0.38	8.8	18.4	2272	0.854	71.1
20	313	67.2	0.41	12.3	17.4	2974	0.894	69.0
30	282	67.2	0.47	15.2	15.4	3505	0.846	68.8
40	272	67.0	0.50	17.2	14.8	3992	0.801	68.8
50	262	66.2	0.53	19.3	15.0	4149	0.850	66.3
60	232	67.7	0.53	19.6	13.6	4323	0.861	65.4
70	218	66.5	0.56	21.9	13.8	4558	0.846	62.0
80	196	69.0	0.63	23.4	12.9	4914	0.790	64.3

All papers were of the glassinelike type after about 50 min. of beating and resembled, in general, papers made from wood holocellulose.

With increase in beating time, the drop in freeness of all pulps was progressive and slow. Fiber flax holocellulose gave the greatest decrease in freeness and the pulp eventually became almost gelatinous. Since hemicellulose fractions are known to increase chemical hydration of pulps (5, 10), it was undoubtedly their presence rather than cutting and fibrillation of the cellulose fibers that contributed to the loss of freeness on beating. The rather light beating treatment used was also a factor in prolonging freeness; however, drastic beating was found to cause excessive cutting of fibers and poor felting qualities in the pulp. The low initial freeness of flax pulp in comparison with that of wheat and oats indicated quite different hydrating properties.

Development of bursting strength was also slow and did not reach a maximum for any pulp in 80 min. Similar results have been reported by Schenck and Kurth (11) for wheat straw holocellulose prepared by the chlorination–ethanolamine procedure. They attributed the slow strength development to the presence of silica in wheat holocellulose. However, this explanation does not appear to be satisfactory, since it was shown in the present work that slow strength development was characteristic of all holocelluloses tested, even though the silica content of wheat holocelluloses was 2.05%, oat 1.14%, and flax nil. Straw holocellulose appeared to exhibit a behavior fundamentally different from that of wood holocellulose, which develops strength rapidly on beating (3, 5). Lovell (8) found, however, that the bursting strength of slash pine holocellulose was high initially and did not increase further. A relatively short beating time of 15 min. was used and there was an extremely sharp drop in freeness. The presence of the hemicellulose fractions is known to increase the hydration of the pulp and contribute to bursting strength. The exact role of the pentosans in binding the cellulose fibers together is unknown but is believed to be a combination of physical and chemical bonding (9, p. 53; 13).

Progressive increase in density with beating was shown for all straws except oats, the increase being greatest in flax. Decrease in bulk in beating pulps is due to a combination of collapse of fibers, partial breaking of fibers, and filling in of the air spaces. Although the crushability of the cellulose fibers was a factor in bulk decrease, the main effect was due to the disintegrating action of the beater. The relatively low densities of straw holocellulose pulps compared with wood should make them useful as 'fillers' in certain kinds of papers made from wood pulp.

The tear strength of all pulps decreased steadily with beating time; this indicated that the fiber lengths were being shortened. Loss of tear strength has been claimed also to indicate ease of hydration. Wood holocellulose from which various hemicelluloses—the easily hydrated fraction of wood—had been removed, showed a progressive resistance to tear (5). The relatively high initial tear resistance of fiber flax holocellulose was due, probably, to the presence of a considerable proportion of coarse fiber bundles in the pulp. The lack of uniformity of texture in the test sheets contributed to low bursting strength and high tear resistance. Flax shives, which consist of relatively short fibers, showed a minimum of tear resistance.

Tensile strength increased with beating for all pulps and indicated progressive increase in fiber-to-fiber bonding. The flax pulps increased steadily in tensile strength over the beating period while wheat and oat straws showed most rapid gain in strength after 20 to 30 min. of beating.

Changes in printing opacities with increased beating time were small and showed little in the way of trends. Lack of uniformity in the formation of many sheets contributed to the irregular results. The only marked decreases in printing opacities were shown after 80 min. of beating (90 min. for wheat holocellulose); this change in property can be correlated with a rise in density for the same beating period. However, no general correlation existed between the progressive increase in density over most of the beating period and printing opacities. Schenck and Kurth (11) have reported little change in opacity (contrast ratio) of wheat straw holocellulose on increased beating.

All brightness values were low when compared with those of bleached wood pulps, which usually are in the range 80 to 90. A slight tendency for brightness to increase with beating time was noted. The brightness of all pulps was much higher than those previously reported for sheets of wheat straw holocellulose (11).

Aging of Straw Holocellulose

Hand sheets made from the straw holocelluloses were observed to undergo color reversion on exposure to light and drying temperatures (90° C.). Houtz and Kurth (5) demonstrated that papers containing hemicellulose fractions aged more rapidly on exposure to ultraviolet light than high alpha-cellulose papers. Rapid color reversion with loss of brightness was found in wheat holocellulose papers by Schenck and Kurth (11).

Quantitative measurement of the 'aging' effect of light was obtained by accelerated tests in a fadeometer. Hand sheets prepared from wheat, oats, and flax pulps that had been beaten for 30 min. were exposed to ultraviolet light from a carbon arc in a humidified fadeometer. The relative humidity was 25% and the temperature 33° to 34° C. Brightness measurements were made on a General Electric reflection meter after various time exposures. The results are given in Table VI. All papers showed a marked loss in bright-

TABLE VI

EFFECT OF AGING BY ULTRAVIOLET LIGHT ON PAPER MADE FROM VARIOUS STRAW
HOLOCELLULOSES

Exposure time, hr.	Brightness, %			
	Wheat	Oats	Fiber flax	Flax shives
0	62.1	58.9	66.9	68.6
1	53.9	53.4	57.9	57.9
2	52.0	53.2	54.8	53.5
4	50.4	49.5	54.1	52.3
6	50.5	49.8	50.9	52.4
8	48.9	49.1	50.9	50.3
12	46.9	46.4	48.2	47.2

ness after one hour's exposure. Thereafter the decrease was much more gradual. The actual loss in brightness was greater for flax straws than either wheat or oats and all losses were much greater than is commonly found in bleached papers from wood pulp.

Since the temperature in the fadeometer was considerably higher than ordinary room temperature, the effect of heat had to be taken into account. Four sheets of each paper were covered with two layers of photographic 'light proof' paper and exposed under the previous conditions for 12 hr. Four uncovered sheets of each paper were exposed to ultraviolet light for the same length of time. The results given in Table VII show that most of

TABLE VII

EFFECT OF AGING BY ULTRAVIOLET LIGHT AND HEAT ON PAPERS MADE FROM VARIOUS STRAW
HOLOCELLULOSES

Conditions	Exposure time, hr.	Brightness, %			
		Wheat	Oats	Fiber flax	Flax shives
Control	0	62.1	58.9	66.9	68.6
Heat	12	60.3	58.1	65.1	67.4
Light + heat	12	46.9	46.4	48.2	47.2

the loss of brightness in all papers was due to the effects of light rather than heat. Launer and Wilson (7) have shown that lignified papers are very unstable to light, especially in the presence of oxygen. Since the holocellulose

contained as high as 4.8% apparent lignin, it may be that the lignin rather than the hemicellulose was responsible for the yellowing. It is significant that the flax papers, which contained more lignin than either wheat or oats, showed the greatest light aging effects.

Uses for Holocellulose Papers

Holocellulose pulps are worthy of commercial interest because of their high yields from woods and straws. Ordinarily about 40% of wood or straw is recovered as useful chemical paper stock, while holocellulose yields are of the order of 65 to 70% of the original material. Most of the gain is due to ·retention of the hemicellulose fraction but a lesser part comes from quantitative preservation of the alpha-cellulose fraction (5). Paper sheets of the glassine type with good physical properties can be readily made. Further chemical treatments can be used to remove hemicellulosic fractions and ultimately yield pure alpha-cellulose. Studies along such lines have already been carried out on wood and sufficiently pure cellulose for the making of derivatives has been obtained (15).

Holocellulose pulps might find uses as glassine or parchment-type papers. Admixture with a proportion of wood pulp with long fibers would make papers such as bond, where hardness, stiffness, and rattle are of value. Additional bleaching would overcome the difficulty of rapid aging. The low density of the straw holocellulose papers would make them valuable as fillers in printing sheets and paperboard. Low tear resistance prohibits their extensive use in paper bags. However, there is little doubt that holocellulose stock would be used in all branches of the paper industry if the cost were competitive with present materials.

At the present time, the cost of making holocellulose by the acid chlorite method is prohibitive owing to the high cost of sodium chlorite. If the price of this chemical could be reduced to about one-quarter of its present figure, then holocellulose pulps would become of immediate interest. No doubt the process would be applied first to wood, because, when available, wood possesses well known advantages over straw as a raw material for pulping.

Acknowledgments

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EFFECT OF PROCESSING AND STORAGE ON THE QUALITY OF GELOSE FROM IRISH MOSS *(CHONDRUS CRISPUS)*[1]

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Abstract

Irish moss (*Chondrus crispus*) from Canada's east coast was used to study possible improvements in the production and storage of gelose. The optimum pH for the extraction of gelose from Irish moss was between 6 and 7. Fine leaf particles, which prevent rapid filtration, were readily removed by supercentrifuging. Comparison of drum drying and drying from the frozen state showed that the former caused a marked lowering of viscosity but had little effect on suspending power or jelly strength. The logarithm of the viscosity determined by means of a MacMichael viscosimeter was related directly to the concentration; therefore, viscosity measurements can be corrected for the moisture content of the samples. The effect of storage temperature on deterioration was greater than the effect of relative humidity. Samples stored at 0° and 40° F. for 12 weeks showed no significant changes in viscosity or suspending power, whereas those stored at 80° and 120° F. deteriorated very rapidly. Material was vacuum ice-dried to 2% moisture without damage but the quality decreased when the extracts were stored at high temperatures.

Introduction

The principal use of the water soluble carbohydrates of Irish moss (*Chondrus crispus*) is in the dairy industry where it serves as a suspending agent in the manufacture of chocolate milk. It also finds considerable use in the pharmaceutical industry as a stabilizer for emulsions and suspensions. In addition to these it serves as a sizing agent in the textile industry, a clarifying agent in the manufacture of beer, a thickener for cold water paints, and a gelling agent in desserts.

Prior to 1939, the bulk of the Irish moss (*C. crispus*) used on this continent was imported from Europe. When this source of supply was cut off by the European war, agar-agar from Japan was substituted where possible. The entry of Japan into the war forced Canada to seek domestic sources of gelling material. Irish moss was available in quantity on Canada's east coast and the processing of this product was examined in these laboratories (2, 6). However, some commercial processors noted that stored dried extracts deteriorated in certain attributes. This paper describes an examination of some of the processing operations and storage conditions that might have affected storage stability.

Analytical Methods

Moisture was determined by drying in air for 16 hr. at 212° F. pH was determined with a Leeds and Northrup pH meter.

A number of methods were tried to establish possible criteria of quality. Reducing sugars (5), free sulphate (8, p. 613), and determination of the gelose content of extracts with benzidine (3) all showed little difference between fresh and stored extracts. Fluorescence values were also useless. However, the commonly used criteria, suspending power, viscosity, and jelly strength, were all found to be useful. The relation of these properties to the uses listed above is obvious.

Suspending Power

The minimum weight, in grams, of dried gelose extract required to give perfect suspension of cocoa in milk was used as an index of suspending power. In the procedure used, various amounts of the dried extracts were weighed into quart cans and 500 gm. milk (2% butterfat), 31.5 gm. sugar, and 5.8 gm. cocoa were added. The containers were closed with screw caps, blocked in a churn, and rotated end over end at about 20 r.p.m. for five minutes at room temperature to mix the ingredients. The churn was then filled with boiling water and rotated for 20 min. The hot water, now about 158° F., was removed, and the milk cooled by two five-minute churnings in water at about 41° F. The contents of the cans were then strained through 80 mesh screens (U.S. Bureau of Standards) into pint milk bottles which were held for 16 to 20 hr. at 40° F. and then for four hours at room temperature.

A suggested alternative method for determining suspending power, described by Rice (7), was examined and found unsatisfactory. Repeated attempts failed to give reproducible results. Rice states that the method is inaccurate in the presence of neutral salts and this may explain some of the difficulty, as these tests were made on commercial material whereas Rice used highly purified extracts. The method is even more cumbersome than the chocolate milk procedure because of the larger number of laboratory manipulations, and numerous attempted modifications to make it more easily applicable were unsuccessful.

Other tests of suspending power were tried but bore no relation to the chocolate milk test. These included: gold numbers (4, p. 58); stabilization of a standard ferric oxide solution against the precipitating action of sodium sulphate; and measurement of the precipitated cocoa in conical-bottomed centrifuge tubes.

Viscosity

The viscosity was determined in a MacMichael viscosimeter with the cup rotating at 20 r.p.m. A portion of dried moss extract (4.00 gm.) was dusted into 200 ml. of distilled water and the mixture was heated in a boiling water bath for 10 min. with stirring. The sol was made up to its original weight with distilled water, and was cooled to 140° F. The viscosity was then determined. All viscosity values are expressed in MacMichael units.

The moisture content of air-dried extract varied from 2 to 30% depending on the relative humidity at which the material was stored. It was, therefore, necessary to correct for the moisture content of each sample so that the values

for all determinations could be brought to a common basis. The concentra-
tion–viscosity relation was investigated on several different lots of material.
Statistical analysis of the results indicated that a correction factor of 0.3940
units of log viscosity for each additional gram of dry matter was generally
applicable. This formula was further tested on several lots of commercial
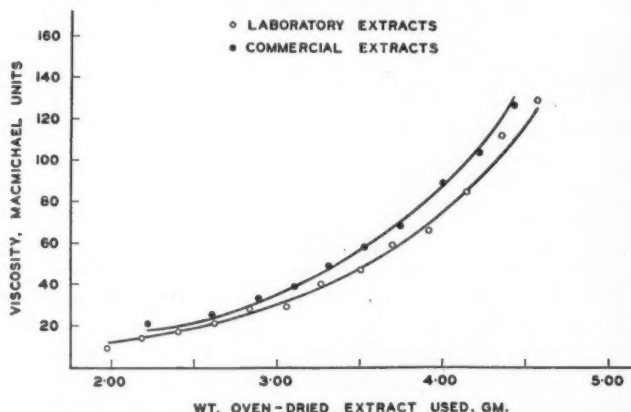material, with the results shown in Fig. 1.

FIG. 1. *The relation between viscosity and concentration of oven-dried extracts of Irish
moss.*

Jelly Strength

The method of preparation of the material was similar to that for the
viscosity test except that 1.50 gm. of dried extract and 100 ml. of distilled
water were used and the sample was cooled to 40° F. and held there for 16 hr.
Jelly strengths were determined at this temperature with a Hall gelometer.
All values are expressed in Hall units, which vary inversely with the jelly
strength.

The Effect of Some Processing Procedures on Quality

pH of Extraction Medium

Buffer solutions (10 liters) 0.05 *M* with respect to phosphate and ranging
in pH from 5.3 to 8.0, prepared as described by Clark (1, p. 81), were used
to extract 300-gm. samples of fully bleached Irish moss. The extracts were
dried from the frozen state (2), ground, and tested. Results of the experiment
are contained in Table I. pH had little effect on the percentage of gelose in
the extracts obtained, but because the more acid solutions gave less viscous
sols, separation from the leaf residue was more complete and higher yields
were obtained from these. There was little effect of pH on suspending power.
Buffer solutions of pH 5.3 and 5.6 resulted in a material with poor viscosity
when made into sols, and solutions of pH 7.4, 7.8, and 8.0 gave materials
that formed gels too weak to be measured. Therefore, the pH for optimum
viscosity lies between 6 and 7.

TABLE I

EFFECT OF pH OF EXTRACTING SOLUTION ON THE QUANTITY AND QUALITY OF GELOSE EXTRACTED FROM IRISH MOSS

pH of extraction solution	Yield, %	Solids in extract, %	Minimum conc. giving complete suspension, gm.	Viscosity of product, MacMichael units	Jelly strength, Hall units	pH of jelly
5.3	43	2.2	0.28	3	2.2	6.0
5.6	51	2.4	0.27	4	2.1.	6.1
6.0	38	2.1	0.28	8	1.9	6.2
6.3	28	1.8	0.26	12	1.7	6.3
6.5	28	1.8	0.28	9	2.0	6.5
6.7	29	1.8	0.30	14	2.2	6.7
6.8	26	1.8	0.30	17	1.8	6.8
7.0	32	1.9	0.30	16	2.4	7.0
7.2	26	1.8	0.35	17	2.1	7.1
7.4	25	1.8	0.30	17	—	7.4
7.8	27	2.0	0.34	24	—	7.6
8.0	28	1.9	0.30	11	—	7.6

Separation of Leaf Fragments

Fulton and Metcalfe (2) suggested the use of a countercurrent extractor to increase the solid content of the gelose solution. However, they were obliged to extract twice to obtain a satisfactory yield of gelose, because, if the leaves were filtered under pressure, many fine leaf fragments remained in the extract and these prevented subsequent filtration. Basket centrifuging did not remove them.

However, the Sharples supercentrifuge was capable of removing a sufficient number of the tiny leaf fragments to render filtration easier. The present procedure consisted of two steps: drainage through a 40 mesh screen (U.S. Bureau of Standards), followed by air pressure filtration (10 lb. per sq. in.). As much of the clear liquid as would readily drain from the leaves was removed first and set aside. Then the portion obtained by pressure filtration was heated to about 194° F. and blown through the supercentrifuge at a rate of 0.3 liter per min. The centrifuged liquid was then combined with the drained liquid before treatment with charcoal and filter-aid (Johns-Manville No. 545). The resulting solutions were clear, odorless, and tasteless, and the yield was as high as that with the countercurrent extraction method (2).

Drying

. Since commercially available moss extracts are usually dried on steam heated drums, a comparison was made between material prepared by the freeze drying method developed in these laboratories (2) and material prepared on a laboratory double-drum drier (steam pressure in the drums, 50 lb. per sq. in., gauge). For both tests the starting material consisted of a sol of Irish moss gelose containing potassium chloride and with a solids concentration

of 4%, obtained by adding previously dried extract. At this concentration, the material dried from the frozen state had fewer ice crystals embedded in the partially dehydrated sheet and it was unnecessary to place crushed ice on the jelly to prevent supercooling.

The results, given in Table II, show that material dried from the frozen state is very little better than drum dried material as a suspending or jelling agent,· but that the former produces sols with much greater viscosity. This

TABLE II

QUALITY TESTS ON DRUM- AND FREEZE-DRIED EXTRACTS OF IRISH MOSS GELOSE, STORED AT 40° F.

Drying method	Storage time, days	Moisture, %	Jelly strength, Hall units	Suspending power, gm.	Viscosity, MacMichael units
Drum	0	12.0	1.20	0.22	15.5
	15	11.5	1.25	0.20	16
Freeze-dried	0	16.0	1.25	0.17	59
	15	15.0	1.30	0.19	44

finding, together with the results given under "pH of Extraction Medium", indicates that suspending power is a relatively stable property of Irish moss gelose, and that viscosity values are not related to indices of suspending power.

The Effect of Storage on Quality

In this experiment both dried extracts prepared in this laboratory and samples of commercial material were studied. Samples were stored at 0°, 40°, 80°, and 120° F. in relative humidities of 0%, 30 to 40%, and 70 to 75%. Each batch was sampled after 1, 2, 4, 8, and 12 weeks of storage.

In view of the variability of the data on viscosity and suspending power, they were transformed to logarithms, plotted against logarithms of time in weeks, and the slopes b of the best fitting straight lines were determined. The regression coefficients and their necessary differences are shown in Table III. There was no significant decrease in the viscosity of the samples stored at 0° and 40° F. However, there was a significant decrease in the viscosity of all samples stored at 80° and 120° F. In the samples stored at 120° F. the relative humidity had significant effects on the rate of viscosity loss. The suspending power did not change during storage at the lower temperatures, the only significant difference being at 120° F. and high relative humidity.

After 12 weeks' storage the reducing sugar (5), free sulphate (8, p. 613), and final moisture contents of each of the storage batches were determined. The pH of 2% solutions of material stored at 0° and 120° F. was also determined. No reducing sugar was found in any of the samples. The results of the remaining measurements, given in Table III, show that free sulphate was

TABLE III

THE QUALITY OF SAMPLES OF IRISH MOSS GELOSE STORED FOR 12 WEEKS AT VARIOUS
TEMPERATURES AND RELATIVE HUMIDITIES

Criteria	Storage Temperature, °F.	0% R.H.*	30–40% R.H.*	70–75% R.H.*	Necessary difference, 5% level
Average decrease of log viscosity per log week, b	0	0.08	0.00	0.04	
	40	0.02	0.01	0.10	0.11
	80	0.19	0.19	0.26	
	120	0.47	0.62	0.76	
Average increase of log suspending power index per log week, b	0	0.05	0.04	0.03	
	40	0.04	0.01	0.01	0.16
	80	0.06	0.10	0.11	
	120	0.12	0.12	0.17	
Final pH, done on 2% solutions	0	5.4	5.5	6.1	
	40	—	—	—	
	80	—	—	—	—
	120	4.9	5.2	5.0	
Final free sulphate content, p.p.m.	0	Trace	Trace	0	
	40	Trace	0	Trace	
	80	Trace	0	0	—
	120	2,690	3,070	4,560	
Final moisture content, %	0	8.5	13.8	23.9	
	40	3.7	12.0	22.2	
	80	1.1	13.9	21.3	
	120	1.0	13.2	21.9	

* Relative humidity.

found only in material stored at 120° F., and that solutions of material stored
at 120° F. were more acid than solutions of material stored at 0° F. With the
exception of samples stored at 0% relative humidity and at the lower tem-
peratures, moisture content had apparently reached equilibrium during the
12 week storage period. Relative humidity had important effects on moisture
content and should preferably be kept below 50% relative humidity. In
general, storage temperatures of 80° F. or higher caused some deterioration
while temperatures of 40° F. or lower were satisfactory.

Samples of commercial material were stored under atmospheres of air,
oxygen, and nitrogen at 140° F. and at relative humidities of 0% and 70 to
75%. These were tested at various intervals and the results, given in
Table IV, show that there was little difference in the rates at which the
samples deteriorated.

TABLE IV

EFFECTS OF STORAGE UNDER DIFFERENT ATMOSPHERES AT 140° F. ON IRISH MOSS GELOSE

Atmosphere	0% R.H.			70 to 75% R.H.		
	Storage time, days	Viscosity, MacMichael units	Suspending power, gm.	Storage time, days	Viscosity, MacMichael units	Suspending power, gm.
Air	0	22.5	0.25	0	22.5	0.25
	3	13.5	—	6	4.5	—
	10	6.0	0.40	12	3.5	—
	20	6.0	—	17	2.5	—
	34	4.0	0.60	20	2.5	0.65
Oxygen	0	22.5	0.25	0	22.5	0.25
	3	12.5	—	6	4.5	—
	10	8.0	—	12	2.5	—
	14	6.5	—	17	2.5	—
	20	6.5	0.30	20	1.0	No suspension
	34	4.0	—			
Nitrogen	0	22.5	0.25	0	22.5	0.25
	3	17.0	—	3	11.5	—
	10	10.0	—	10	4.0	—
	14	8.5	—	14	2.5	—
	20	8.5	0.40	20	2.0	No suspension
	34	2.5	—	34	0	—

It was thought that loss of viscosity at high temperatures might be due to the initial moisture contents of the samples (about 10%). This was not evident in the present work as it required approximately two weeks to lower the moisture content of samples stored at 120° F. and 0% relative humidity to 2%. By that time a considerable amount of deterioration had already taken place. Accordingly, samples of commercial material were dried at 104°, 122°, and 140° F. under partial vacuum (25 in.). The materials were tested after 1, 2, 4, 6, 24, and 48 hr. of drying. The results in Table V show a marked decrease in viscosity as moisture was removed from the sample.

TABLE V

EFFECT OF DRYING TEMPERATURE ON VISCOSITY OF EXTRACTED GELOSE

Drying time, hr.	104° F.		122° F.		140° F.	
	Viscosity, MacMichael units	Moisture, %	Viscosity, MacMichael units	Moisture, %	Viscosity, MacMichael units	Moisture, %
Original material	80*	10.0	80	10.0	80	10.0
1	78	9.5	81	7.9	81	8.0
2	78	8.7	80	6.0	72	7.0
4	74	7.1	65	4.3	69	5.3
6	—	—	67	4.3	63	4.1
24	74	4.0	67	3.8	47	2.8
48	67	4.5	—	—	—	—

* All viscosity values were corrected for moisture content of sample.

When high temperature drying was found to be undesirable, a sample of dried extract was held for two weeks at 0° F. under partial vacuum (25 in.). The product then had 2% moisture and a viscosity equal to that of the original material. Portions of the original material and this dried product were then stored over phosphorus pentoxide at 120° F. The moisture content of both materials gradually decreased to zero and both decreased in viscosity. It appears, therefore, that deterioration at high temperatures is not due to the initial moisture content of the material.

Discussion

The present work shows that the suspending power and the viscosity of sols from Irish moss gelose prepared by different procedures are not related. Gelose finds its main use as a suspending agent in chocolate milk, and for this purpose the method of preparation does not appear to be important, since suspending power is a relatively stable property. For other uses (e.g., thickening agent in pharmaceuticals, cold water paints, etc.) where high viscosity is desired, the method of preparation may be extremely important, since viscosity is substantially affected by the method of preparation. High temperature drying appears to be particularly detrimental. The results indicate that products with high viscosity can be obtained by drying and concentrating by a freezing process, and that these extracts should preferably be stored at temperatures below 40° F.

While these experiments were not designed to determine the fundamental nature of the deterioration, it might be observed that, since the deterioration was more pronounced in samples of high moisture content and was associated with an increase in free sulphate, the changes resulting in a reduction of viscosity may be of a hydrolytic character.

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PRODUCTION AND PROPERTIES OF 2,3-BUTANEDIOL

XXVI. VAPOR-LIQUID EQUILIBRIA OF THE SYSTEM *levo-*2,3-BUTANEDIOL – WATER[1]

By R. V. Tomkins[2], J. A. Wheat[2], and D. W. Stranks[3]

Abstract

A modified Othmer equilibrium still was used to obtain vapor–liquid equilibrium data for the *levo*-2,3-butanediol–water system at 14.7, 45, and 75 p.s.i. absolute. Comparison with similar data reported in the literature for the *meso*-2,3-butanediol–water system showed a greater volatility for the *levo*-isomer. There is an inflection in the equilibrium curves at lower diol concentrations.

Introduction

The design and operation of a pilot plant for the recovery of *levo*-2,3-butanediol from wheat mashes fermented by *Aerobacillus polymyxa* required information on the vapor–liquid equilibrium relations of the diol–water system. In particular, the equilibria data at elevated pressures were needed for evaluation of steam stripping of diol from concentrated mash. Knowlton, Schieltz, and Macmillan (3) have reported on this system at absolute pressures of 200, 400, 600 and 800 mm. of mercury. Blom *et al.* (1) have investigated the *meso*-2,3-butanediol – water system over a pressure range from 2.45 to 80 p.s.i. absolute, and Othmer and colleagues (8) from 200 to 760 mm. of mercury absolute. The present work with the *levo*-isomer includes data at 14.7, 45, and 75 p.s.i. absolute. The diol concentrations encountered in stripping operations are well within the range investigated.

Materials and Methods

levo-2,3-Butanediol

The butanediol used for this work was produced in the pilot plant of the National Research Laboratories by fermentation of wheat mash by *A. polymyxa*. The crude material was purified by two rectifications at 3 in. of mercury absolute, the first over sodium hydroxide to remove free and combined acids. The product was 97% diol, the remainder being water. The butanediol produced by this organism has been shown by Neish (5) to consist of the *levo*-isomer only.

Analytical Methods

Chemical analyses were used rather than physical measurements because of greater accuracy in the low diol concentration range. Solutions containing up to 90% diol were analyzed by the University of Wisconsin periodate method (4), the butanol extraction being omitted, as no interfering substances were present. The water content of solutions containing from 70 to 100% diol

was determined with Karl Fischer reagent.   In the range where both determinations were performed a mean value was obtained.   The accuracy of both methods is about $\pm$ 0.5%.   Hypodermic syringes were used as weight pipettes for handling the concentrated solutions, to prevent absorption of atmospheric moisture.

Apparatus

The equilibrium still used for this work was a modification of the glass Othmer still (6), constructed of brass pipe fittings to allow use at elevated pressures.   A sketch including pertinent details and dimensions is shown in Fig. 1.   The vapor jacket and vapor line to the condenser were insulated
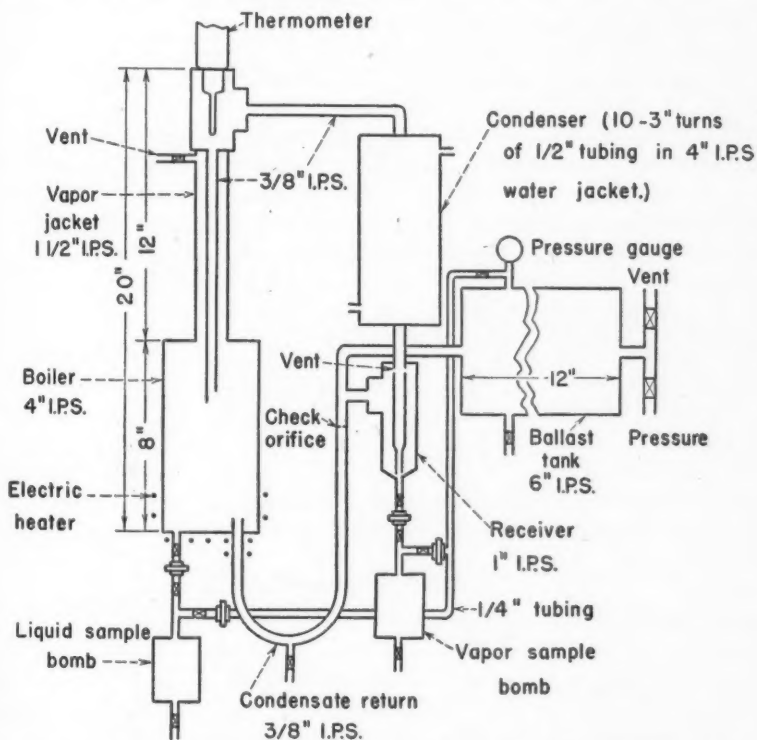

FIG. 1.   Sketch of equilibrium still and auxiliary equipment, approximately to scale.

with about 2 in. of asbestos and 1 in. of 85% magnesia.   The temperature of the vapors was measured with a Taylor industrial thermometer calibrated in 2° C. divisions and read to the nearest 0.5° C.   This was used to aid in operating the still rather than to obtain boiling point data.   The thermometer body was insulated with 1 in. of corrugated asbestos.   The check orifice (3/32 in.) prevented surges in the return line.   The voltage applied to an

external electric element (32 ft. of 16 gauge Chromel wire) was controlled by a Variac transformer. Nitrogen was used for pressure operation, and the pressure was read on a calibrated Bourdon gauge.

Since this still was constructed, Othmer and Morley (7) have published a description of similar apparatus.

Operation

Certain precautions must be observed when operating the still to avoid false results. Refluxing must be prevented or the vapor sample will contain too much of the more volatile component. The insulation on the apparatus was sufficient to reduce condensation to a negligible value relative to the boiling rates used. Similarly incorrect values will be obtained if insufficient cycles occur in the condensate system because of too short a boiling period or too low a boiling rate. Low concentrations of the more volatile component in the vapor will be observed if entrainment results from too high a boiling rate.

The following experiment was undertaken to determine operating conditions at which these errors would be minimized. A series of distillations was carried on at atmospheric pressure, the boiling rate being varied. A charge of 850 ml. of approximately 20 weight % diol was used. In this apparatus, the liquid hold-up was larger than is common, and a five hour boiling period was used to assure that equilibrium would be established. The samples were analyzed and the vapor compositions calculated to a basis of 20.0 weight % diol in the liquid*. The results are presented graphically in Fig. 2.
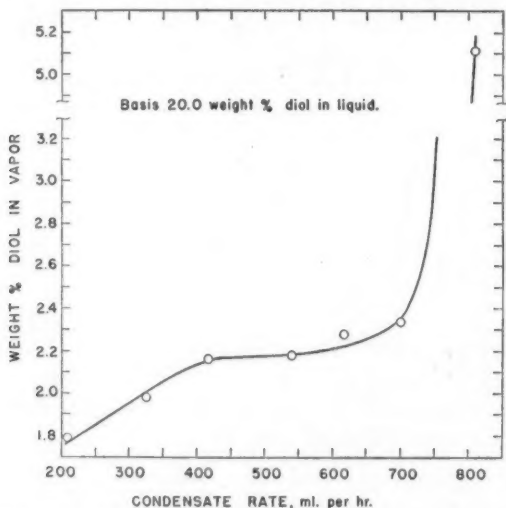

FIG. 2. *Effect of boiling rate on apparent vapor composition.*

* *The calculations were made by considering the slope of the weight per cent diol in vapor vs. weight per cent diol in liquid curve to be 0.10 in the narrow range from 20.3 to 22.3 weight % diol into which the liquid samples fell.*

Below 400 ml. per hr., equilibrium apparently had not been established. Between 400 and 550 ml. per hr. the vapor composition did not change significantly, and this is the range in which the still was subsequently operated. Above this rate, entrainment caused excessively high values for the diol concentration in the vapor. At higher pressures the same rate of boiling can be used, as the same number of cycles will occur in the condensate system, and the higher pressure reduces vapor velocity and hence entrainment. Excessively long boiling periods would have to be used for vacuum work, as the boiling rate has to be reduced greatly to prevent entrainment. Also, at very low boiling rates, there is danger of the small amount of reflux caused by heat loss having a significant effect on the distillation.

As the condensate receiver holds about 50 ml., the boiling rates selected result in 45 to 55 cycles during the five hour boiling period.

Samples were taken at superatmospheric pressure by means of bombs arranged, as shown in Fig. 1, so the pressure in the bomb was the same as that in the still. The liquid sample line was cooled when samples were taken to prevent flashing and consequent errors.

The heat input required at different pressure and concentration levels was determined by preliminary experiments, and the rate of boiling was checked at the end of each determination.

For a typical test, the 850 ml. of solution was charged to the still and brought to boiling with the vent open to allow fixed gases to escape. The system was then closed and nitrogen admitted slowly, so that boiling was not stopped, until the desired pressure was reached. The still was then left in operation for five hours. The valves from the bombs to still and condensate receiver were opened simultaneously, left open for about 30 sec., and then closed. All valves to the bombs were then closed; the bombs were removed and cooled; the pressure was released; and samples were removed and analyzed.

Experimental Results

The experimental data obtained are given in Table I, and presented on logarithmic scales (to spread the points at low diol concentrations) in Fig. 3. The conventional y–x diagram (Fig. 4) showing the equilibrium at atmospheric pressure also includes an enlarged portion at the three pressures investigated for diol concentrations below 20 mole %. It is obvious that there is an inflection at higher water concentrations, resulting in a reverse curve similar to that of the ethanol–water system, but very much farther removed from the $y=x$ line. The data are not correlated by the Van Laar equation (2) or the equations of White (10).

Fig. 5 relates vapor composition to absolute pressure at various liquid composition levels. The points fall on approximately straight lines up to 10 mole % diol in the liquid. Interpolation and extrapolation to lower

TABLE I

LIQUID AND VAPOR COMPOSITION OF *levo*-2,3-BUTANEDIOL SOLUTIONS

Pressure, p.s.i. absolute	Temperature, °C.	Weight % diol in		Mole % diol in	
		Liquid	Vapor	Liquid	Vapor
14.7	100	0.567	0.0608	0.114	0.0122
	100	2.18	0.291	0.444	0.0584
	100	5.30	0.734	1.105	0.1475
	100.5	11.00	1.30	2.40	0.263
	101	20.8	2.27	4.98	0.465
	101.5	38.5	3.67	11.11	0.753
	102.5	58.5	5.38	22.0	1.122
	105.5	74.3	8.47	36.7	1.815
	109	86.0	17.35	55.1	4.03
	114	88.1	19.9	59.6	4.74
	126	94.3	37.4	76.8	10.67
	138	96.8	55.2	85.6	19.8
	141	97.1	59.2	86.8	22.5
45	134.5	0.535	0.155	0.1075	0.0310
	134.5	1.373	0.352	0.278	0.0707
	134.5	5.70	1.328	1.192	0.268
	134.5	6.71	1.563	1.418	0.317
	135	14.0	3.30	3.15	0.676
	135.5	20.8	4.43	4.98	0.919
	136	39.0	6.90	11.32	0.460
	136.5	49.6	7.73	16.45	1.650
75	153	0.642	0.233	0.1290	0.0467
	153	1.946	0.682	0.395	0.137
	153.5	6.60	2.21	1.394	0.450
	154	14.55	3.59	3.29	0.739
	154.5	20.0	4.57	4.77	0.950
	155	37.0	7.09	10.50	1.500
	157.5	67.5	13.22	29.4	2.96

pressures appear justified, judging by the work of Blom *et al.* (1). Their results for the *meso*-diol are also shown on this figure for comparison. As would be expected from the difference in boiling points of the isomers the *levo*- shows greater volatility than the *meso*-, the difference being more pronounced at lower diol concentrations. The equilibria at atmospheric pressure are not in accord with the data of Knowlton *et al.* below 50 weight %. However as these workers used boiling point to determine composition, and the change of boiling point with composition is very small at low diol concentrations, it is believed that the present work using chemical analysis to determine composition is more reliable.
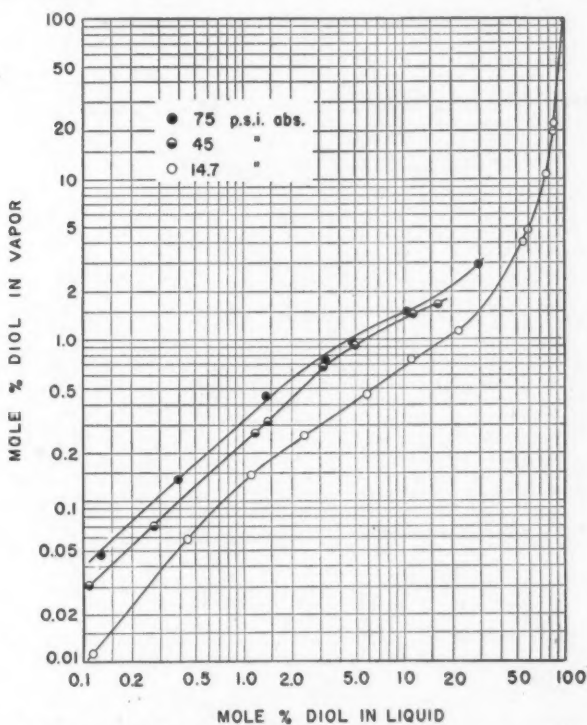
FIG. 3.   Vapor–liquid equilibria for levo-2,3-butanediol, plotted on a logarithmic scale.
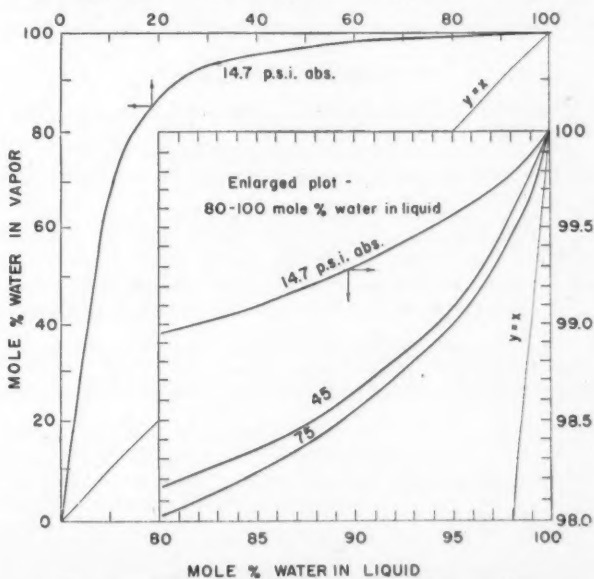

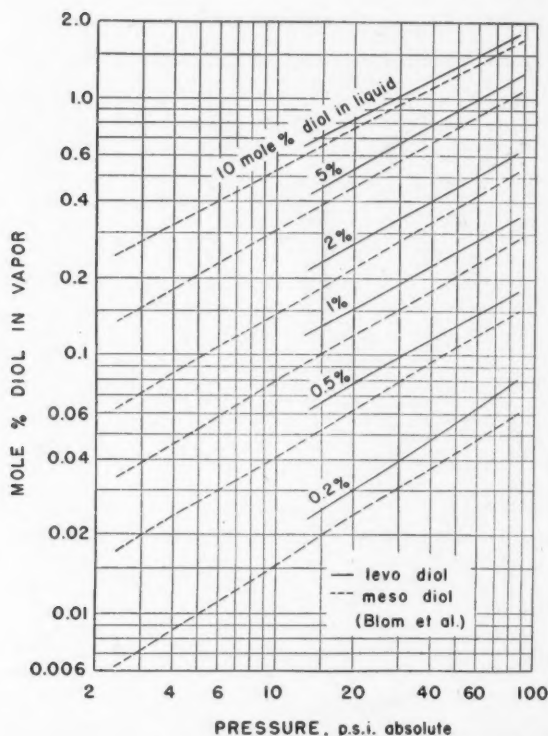FIG. 4.   Vapor–liquid equilibria of levo-2,3-butanediol.

FIG. 5.   Vapor–liquid equilibria of levo- and meso-2,3-butanediol (1), at various liquid compositions, showing effect of pressure on vapor composition.

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